Joint Test Plan to Identify the Gaseous By-Products of CH₃I Loading on AgZ

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SUMMARY

The objective of this test plan is to describe research to determine the gaseous by-products of the adsorption of CH_3I on hydrogen reduced silver exchanged mordenite (AgZ).

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ACRONYMS

AgZ Silver exchanged mordenite

ANL Argonne National Laboratory

APS Advanced Photon Source

DRIFT diffuse reflectance infrared Fourier transformed spectroscopy

DOG dissolver off-gas

DP dew point

FTIR Fourier transform infrared spectroscopy

GC/ECD gas chromatography – electron capture detector

ICP-MS inductively coupled plasma mass spectrometry

INL Idaho National Laboratory

IR infrared spectroscopy

ORNL Oak Ridge National Laboratory

PDF pair distribution fuction

PNNL Pacific Northwest National Laboratory

SNL Sandia National Laboratory

VOG vessel off-gas

XRF X-ray fluorescence

SEPARATIONS AND WASTEFORM CAMPAIGN

JOINT TEST PLAN TO IDENTIFY THE GASEOUS BY-PRODUCTS OF CH₃I LOADING ON AGZ

1. OBJECTIVE

The objective of this test plan is to describe research to determine the gaseous by-products of the adsorption of CH₃I on hydrogen reduced silver exchanged mordenite (AgZ).

2. BACKGROUND

In FY10 INL conducted three breakthrough runs using AgZ. During the course of these tests elemental iodine was observed in the effluent from the bed. The only source of iodine in the system was the CH_3I in the feed gas. It was hypothesized that the elemental iodine was generated within the sorbent bed, presumably from a reaction likely catalyzed by silver mordenite. It was also observed that the levels of CH_3I and I_2 in the effluent did not rise in concert, i.e., the ratio of the CH_3I in the effluent decreased from \sim 96% to 3-5% over the course of the run (Haefner, 2010).

This behavior does not appear to have been reported previously nor has it been independently confirmed. Previous work at PNNL, INL and ORNL conducted in the late 1970s and early 1980s also focused on the adsorption of CH₃I on AgZ as this was thought to pose a greater challenge to the iodine sorption media than elemental iodine. However, these tests did not examine the effluent gas in great detail.

3. DATA GAP ANALYSIS

A number of questions have been posed by the observed behavior and are presented in Table 1. This table also identifies relevant past work and possible approaches to develop answers to the seven main questions.

The two initial key questions that need to be addressed from this list of seven main questions are:

- 1. Is elemental iodine observed in the effluent? This will require duplicating the run from FY10 with sufficient sampling and analysis to confirm or refute the previous observation. Subquestions include:
 - a. What other iodine species are in the effluent?
 - b. What organic compounds are in the effluent?
- 2. If the reported behavior is confirmed, then what is the origin of the elemental iodine? Subquestions include:
 - a. Is this a gas-gas reaction?
 - b. Is this a result of the iodine capture?
 - c. Is this a result of the substrate?

Table 1. Fixed b Phenomenon or question	ed methyl io Priority	Fixed bed methyl iodide adsorption behavior and questions Priority Initial answers/comments from past work CH.1 converted to 1, by NO or NO.: improves tramping.	Proposed options to address the questions
I happens to organic todude? React in gas stream prior to interaction with solid sorbent? Impact of NO, NO ₂ , H ₂ O, O ₂ React because of interaction with solid sorbent?	C	CH ₃ I converted to 1 ₂ by NO or NO ₂ ; improves trapping efficiency (Scheele 1983); {Note: this is not consistent with statement from Scheele 1983 below in Question 4 about NO}.	 a. (1) HSC Chemistry cases (INL) a. (2) Ambient and elevated T tests with CH₃1 gas mixtures w/, w/o NO, NO₂,
Impact of NO, NO ₂ , H ₂ O, O ₂ Impact of the solid sorbent – Ag catalytic? Different sorbents? Iodine is separated from organic moiety after physisorption prior to chemisorption?	OOZ Z	CH ₃ I converted to I ₂ such that the determination of capture efficiency of total iodine must account for both CH ₃ I and (I ₂ +HI) in the effluent gas. At initial breakthrough, most (95%) of the small amount of	H ₂ O, O ₂ , analyze for CH ₃ I+ (I ₂ +HI); no sorbent (INL). b. (I) Deep-bed tests w/ CH ₃ I, I ₂ , HI gas analysis, w/ and w/o Ag (INL).
	:	breakthrough 1s due to C.H.3.f. out as breakthrough continues and efficiency decreases, the amount of breakthrough (1 ₂ +HI) rises faster than the amount of breakthrough C.H.3.f. reaching 97% of total iodine breakthrough. (Haefner 2010).	
is ultimate fate of the organic moiety? Adsorbs onto sorbent? As what species? Is released or remains in gas stream? What species?	M L	Donner and Tamberg proposed CH ₃ OH (methanol) and CH ₃ OCH ₃ (dimethyl ether) as possible organic reaction products (Scheele 1983). Dimethyl ether detected at outlet (prior work cited in Scheele).	HSC Chemistry (INL?). Deep-bed tests – GC, MS analysis of gas, mass of sorbent, ultimate analysis of sorbent (INL).
		GC peak matched retention time of methanol (Haefner 2010).	
is the form of adsorbed iodine? AgI Other species Physisorbed vs chemisorbed and different forms of physisorption – surface vs pore, etc.	ннн	AgI or AgIO ₃ based on thermodynamic equilibrium, possibly a silver-iodine complex speculated based on empirical results (Scheele). (But the empirical results could also be explained by physisorption/desorption of a portion of the total iodine.)	HSC Chemistry (INL?).
4. What are potential adsorption efficiencies and mass transfer zone depths for organic iodide?	i	Trapping efficiency higher with H ₂ , and no NO (Scheele 1983).	1. Deep-bed tests – 1 AgZ, 1 Aerogel, selected gas conditions (INL).
	O	CH ₃ I capture (is this efficiency or capacity?). No impact of O ₂ , improves at higher T from $100\text{-}200^{\circ}\text{C}$, improves at higher H ₂ O from to $0.01\text{-}1.2$ vol %; (prior work cited in Scheele 1983).	
5. What are potential adsorption capacities and Ag utilizations for organic iodide for base case AgZ and Ag-functionalized Aerogel Impact of NO, NO ₂ , H ₂ O, O ₂ on AgZ Impact of NO NO ₂ , H ₂ O, O ₃ on Ag-functionalized Aerogel	H 1	Potential maximum capacities and Ag utilizations were not demonstrated by Scheele 1983, Haefner 2010, Jubin 1980, 1982, or Murphy 1977 because those tests stopped at or shortly after an arbitrary decrease in sorntion	Deep-bed tests – 1 AgZ, 1 Aerogel, selected gas conditions (INL). Thin-bed tests (ORNL). Aeropel tests (PNNL).
	1	efficiency (DF = 1,000 for Jubin 1980 or 1982; DF=100 for Scheele 1983; 250 ppb CH ₃ I in effluent stream for Haefner 2010).	rmi Ag
		NO improves 1 ₂ loading; NO ₂ decreases 1 ₂ loading; water up to 5.5 vol % has negligible effect on loading; Temp between 100-250°C has negligible effect on loading (Murphy 1977).	
		CH ₃ 1 at ~170 ppmy; No impact of NO or NO ₂ on CH ₃ 1 loading; H ₂ O up to 4.8 vol % improves CH ₃ I loading; T up to 225°C improves loading but also increases depth of	

MTZ; (Jubin 1980, 1982). CH ₃ I at ~300 ppm; NO, NO ₂ at 0, ~1,000, and ~20,000 ppm; H ₂ O at 0.01% and 1.2%; used on-line GC/PID for measuring CH ₃ I; starch to indicate 1 ₂ presence; measured iodine in sorbent using XRF. Iodine capacities measured up to 21.7 wt% (Scheele 1983). CH ₃ I at 25-34 ppm; 500-800 ppm NO, NO ₂ ; 1.5-2% H ₂ O; 150°C; 4.3 m/min superficial velocity; 5.5-7.1% iodine loading. On-line GC/ECD detection of CH ₃ I, iodine loading determined gravimetrically (Haefner 2010).	Thin-bed tests (ORNL)?	 a. Smaller [20.40 mesh (0.042-0.0841 cm)] better than larger [0.16 cm extrudate] particles (Scheele 1983) b. Ag'Z better than AgZ (Scheele 1983); Ag'Z 2x higher capacity than AgZ, up to 17.1% 12 loading at DF=1,000 (Murphy 1977); 12.7 wt% for CH₃ I (Jubin 1980, 1982). Higher reducing T from 200-500°C and longer times up to 48 hr increase size of Ag nodules and reduce loading capacity; but partially exchanged Ag Z increased Ag utilization (presumably due to smaller Ag nodules?) (Jubin 1980 or 1982). c. Aging decreases 12 sorption capacity of H-reduced AgZ (Bruffey 2012, Jubin 2012). d. Temps up to 200 C and lower velocities down to 3.75 m/min improve trapping efficiency (Scheele 1983).
	M	Σ н∑н
	6. Kinetic data (effective diffusivity)	7. How do adsorption efficiencies, mass transfer zone, capacities, and Ag utilization vary for: a. Different AgZs and Aerogels – structures, elements, Ag levels, surface areas / pore structures b. Reduced vs non-reduced and method of reduction c. Different aging of Ag-reduced sorbents d. Different sorption T, superficial velocity

Note: Priority codes:
C Critical
H High
M Medium
L Low

Table 1 also shows a number of other questions that need to be answered to understand the mechanism and impact of this behavior. The initial confirmatory phase will be covered within the FY13 scope of work. Additional phases are proposed to address these remaining questions in FY14 and possibly FY15.

The test plan presented below details the Phase I tests needed to identify the gaseous by-products that arise from the adsorption of CH₃I by AgZ. The subsequent phases are needed to address the remaining questions and are included for completeness, but in less detail. The completion of all phases is needed to gain fundamental engineering data associated with the adsorption of organic iodide compounds on silver-containing sorbents.

4. TEST PLAN

Phase II and Phase III tests are less defined and will be revised and refined based on a review of the Phase I test results. Conceptually, Phase II and Phase III portions of this test plan are designed to provide significantly more insight into the mechanisms associated with the adsorption and reaction / decomposition of CH₃I and other organic iodides on AgZ and other iodine sorbents. These tests should provide data to support engineering calculations that are needed to design iodine capture systems which efficiently and reliably remove organic iodides

Note: Question numbers follow specific test numbers shown in Table 1.

- 1. Phase I Testing Confirm previous observations and identify primary factors.
 - a. Chemical equilibrium calculations HSC Chemistry or some other model of what might be expected in gas-phase and gas-solid phase reactions (INL to do gas-solid reactions; ORNL to do gas gas reactions.) (questions 1, 2b)
 - b. Deep-Bed Tests at INL
 - i. Determine stability of gas phase samples. (INL / PNNL / others?)
 - ii. Blank tests no sorbent, 150 °C, with and w/o NO, NO₂, H₂O, to assess gas-phase reactions (Question 1a)
 - 1. Test 1:
 - a. 150 °C.
 - b. superficial velocity 4.3 m/sec,
 - c. 33 ppm CH₃I,
 - d. 2 wt% water,
 - e. 833 ppm NO,
 - f. 833 ppm NO₂.
 - 2. Test 2 if elemental iodine observed in Test 1 in this series, perform a test without H₂O and NO_x:
 - a. 150 °C,
 - b. superficial velocity 4.3 m/sec,
 - c. 33 ppm CH₃I,
 - d. \sim 30 ppm water (-70 °C dew point [DP]),
 - e. 0 ppm NO,
 - f. 0 ppm NO_2
 - 3. Test 3 if elemental iodine observed in Test 1 in this series, perform a test without H₂O:
 - a. 150 °C,

- b. superficial velocity 4.3 m/sec,
- c. 33 ppm CH₃I,
- d. \sim 30 ppm water (-70 °C DP),
- e. 833 ppm NO,
- f. 833 ppm NO₂
- 4. Inlet and outlet gas streams will be analyzed to measure CH₃I, I₂, and to the extent practical with existing available instrumentation, other likely gaseous reaction products, in near real time using FTIR, GC-MS, ICP-MS, etc.
- 5. ORNL will have capabilities to run at % levels of NO and NO₂ and could complement these tests.
- iii. Replicate CH₃I loading on deep bed to confirm presence of elemental iodine in effluent. Goal: Determine presence / absence of I₂ and / or CH₃I at intermediate points in bed. First branch point Is I₂ observed. If no then the primary purpose of this test plan has been achieved. (question 1b, 1c)
 - 1. Test 1:
 - a. 150 °C,
 - b. superficial velocity 4.3 m/sec,
 - c. 33 ppm CH₃I,
 - d. 2 wt% water,
 - e. 833 ppm NO,
 - f. 833 ppm NO₂.
 - 2. Test 2 if elemental Iodine observed in Test 1 in this series, perform a test without H_2O and NO_x :
 - a. 150 °C,
 - b. superficial velocity 4.3 m/sec,
 - c. 33 ppm CH₃I,
 - d. \sim 30 ppm water (-70 °C DP),
 - e. 0 ppm NO,
 - f. 0 ppm NO_2
 - 3. Test 3 if elemental Iodine observed in Test 1 in this series, perform a test without H₂O:
 - a. 150 °C,
 - b. superficial velocity 4.3 m/sec,
 - c. 33 ppm CH₃I,
 - d. \sim 30 ppm water (-70 °C DP),
 - e. 833 ppm NO,
 - f. 833 ppm NO₂
 - 4. Inlet and outlet gas streams should be analyzed to measure CH₃I, I₂, and to the extent practical with existing available instrumentation, other likely gaseous reaction products, in near real time with available tools including FTIR, GC-MS, ICP-MS, etc.
 - 5. ORNL will have capabilities to run at % levels of NO and NO $_2$ and could complement these tests.

- 6. Determine if there are temporal changes in form, i.e., does I₂ at given distance in bed increase with run time or is it fixed with respect to adsorption front? This may require a slight change in design of the deep bed system, such as six 1.27 cm deep beds instead of beds of varying depth, for example. The actual configuration should be developed following assessment of results of the initial tests.
- iv. Repeat tests with Ag-free sorbent to determine if effect detected in 1.a is result of the presence of Ag or merely the result of the substrate. Goal: Determine if observed behavior is the same or different as with AgZ. (question 1b, 1c)
 - 1. Repeat tests in 1.b.iii with NaZ or other non Ag media. If effect is observed conduct a follow-on test with alternate zeolite.
- v. Characterize the form / species of iodine in the gas stream that passes between bed sections. (questions 1c, 2b)
 - 1. Potential sample analysis techniques include: FTIR, GC, ICP-MS.
- c. Single pellet tests at ORNL These tests will utilize the test protocol established in the joint test plan for thin bed and deep bed testing of iodine sorbents (Jubin 2012b). A portion of the materials produced in this series of tests will be used in the analysis performed in section 1.c of this plan.
 - i. General test conditions to be used on this series of tests:
 - 1. Test 1:
 - a. 150 °C,
 - b. superficial velocity 4.3 m/sec,
 - c. $33 \text{ ppm CH}_3\text{I or } 25 \text{ ppm I}_2$,
 - d. 2 wt% water,
 - e. 833 ppm NO,
 - f. 833 ppm NO₂.
 - 2. Test 2:
 - a. 150 °C,
 - b. superficial velocity 4.3 m/sec,
 - c. 33 ppm CH₃I,
 - d. \sim 30 ppm water (-70 °C DP),
 - e. 833 ppm NO,
 - f. 833 ppm NO₂.
 - 3. Test 3:
 - a. 150 °C.
 - b. superficial velocity 4.3 m/sec,
 - c. 33 ppm CH₃I,
 - d. \sim 30 ppm water (-70 °C DP),
 - e. 0 ppm NO,
 - f. 0 ppm NO_2 .
 - ii. Determine which iodine compounds limit the adsorption process and the impact of operational conditions on limits
 - 1. Determine the maximum capacity for inorganic iodine on the NaZ
 - a. How much is chemisorption; Ag-free sorbent

- b. How much is physisorption; Ag-free sorbent
- 2. Determine the maximum capacity for CH₃I
 - a. How much is chemisorption; Ag-free sorbent (question 1c, 1d, 3, 6)
 - b. How much is physisorption; Ag-free sorbent (question 1c, 1d, 3, 6)
- 3. Determine the maximum capacity for inorganic iodine on the AgZ
 - a. How much is chemisorption; Ag sorbent
 - b. How much is physisorption; Ag sorbent
- 4. Determine the maximum capacity for CH₃I
 - a. How much is chemisorption; Ag sorbent (question 1c, 1d, 3, 6)
 - b. How much is physisorption; Ag sorbent (question 1c, 1d, 3, 6)
- d. Structural studies (PDF) at SNL/ANL/APS on samples prepared at INL and ORNL. Goal is to identify if the adsorption of CH₃I occurs at the same sites as I₂.
 - i. Static tests to see where CH₃I adsorbs on AgZ (question 3c)
- 2. Phase II Testing to be carried out if Phase I tests confirm the presence of both I₂ and CH₃I in the gas phase from the AgZ.
 - a. Deep bed tests at INL
 - i. Initial tests with inorganic iodine (I₂ and HI) to determine a set of reference data. HI could be considered if and when the need is established to be prototypic and a suitable generator is available
 - 1. Ag-free sorbent
 - 2. Ag-loaded sorbent
 - ii. Initial data need to indicate that the material has sufficient decontamination and capacity to warrant further testing
 - 1. Determine DF how is this affect by operating conditions for CH₃I adsorption.
 - 2. Determine MTZ how is this affect by operating conditions for CH₃I adsorption
 - iii. Tests with CH₃I and mixtures of CH₃I, I₂, and HI at prototypic concentrations and higher concentrations
 - 1. Characterize the gases passing between bed sections
 - 2. Characterize the solids after reactions have run their course
 - b. Single pellet tests at ORNL
 - 1. Determine the maximum capacity for CH₃I and mixtures of organic and inorganic iodine
 - a. Impact of H₂O, NO, NO₂ on CH₃I adsorption. (question 1b, 4, 5, 6, 7)
 - b. Determine the effects on the solid sorbent
 - c. Studies on AgZ with variations in streams to monitor sorption in real time. (CH₃I, H₂O, NO, NO₂, etc.) using in-Situ DRIFT/PDF (IR & synchrotron)
 - i. Impact of H₂O, NO, NO₂ on CH₃I adsorption. (questions 3c and 5)
 - d. Structural studies (PDF) at SNL/ANL/APS on samples prepared by INL and ORNL
 - i. Static tests to see where CH₃I adsorbs on AgZ (question 3c)

- 3. Phase III Testing Expanded evaluations into prototypic conditions for DOG and VOG
 - a. For the materials that meet the minimums above, perform tests at INL and ORNL with prototypic non-iodine gas mixtures (air, humidity, mixtures of NO_x, other off-gas components)
 - i. Perform deep-bed tests at INL with prototypic gas streams and iodine concentrations which are most likely mixtures of inorganic and organic compounds
 - 1. Characterize the solids from these tests
 - 2. Characterize the changes in the component concentrations in these prototypic gases when they pass through the solid sorbent; Ag-free sorbent
 - ii. Perform capacity tests at ORNL with prototypic gas streams and iodine concentrations
 - 1. Characterize the solids from these tests
 - 2. Characterize the changes in the component concentrations in these prototypic gases when they pass through the solid sorbent; Ag-free sorbent
 - iii. Perform 'aging' tests at ORNL with prototypic gas streams
 - 1. Characterize the solids from these tests
 - 2. Characterize the changes in the component concentrations in these prototypic gases when they pass through the solid sorbent; Ag-free sorbent

5. REFERENCES:

Bruffey 2012: Bruffey, S. H., K. K. Anderson, R. T. Jubin, and J. F. Walker, Jr. 2012. *Aging and Iodine Loading of Silver-functionalized Aerogels*, FCRD-SWF-2012-000256, August 31, 2012.

Haefner 2010: Haefner, Daryl and Tony Watson, "Summary of FY 2010 Iodine Capture Studies at the INL," INL/EXT-10-19657, August 2010.

Jubin 1980: Jubin, R.T., "Organic Iodine Removal from Simulated Dissolver Offgas Systems Using Silver-Exchanged Mordenite," Proceedings of the 17th Air Cleaning Conference, Conf-820833-12, 1982.

Jubin 1982: Jubin, R.T., "Organic Iodine Removal from Simulated Dissolver Offgas Systems Using Partially Exchanged Silver Mordenite," Proceedings of the 17th Air Cleaning Conference, Conf-820833-12, 1982.

Jubin 2012a: Jubin, R.T., "Summary of FY-12 Off-gas Sigma Team Activities," FCR&D-SWF-2012-000331, September 21, 2012.

Jubin 2012b: Jubin, R.T., N. R. Soelberg, "Joint Test Plan for the Thin Bed and Deep Bed Testing of Iodine Sorbents," FCR&D-SWF-2013-000031, November 15, 2012

Murphy 1977: Murphy, L.P., B.A. Staples, and T.R. Thomas, "The Development of AgoZ for Bulk ¹²⁹I Removal from Nuclear Processing Plants and PbX for ¹²⁹I Storage," ICP-1135, INEL, 1977.

Scheele 1983: Scheele, R.D., L.L Burger, and C.L. Matsuzaki, "Methyl Iodide Sorption by Reduced Silver Mordenite," PNL-4489, UC-70, June 1983.